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ART. I.—*Kaolinised Granodiorite in the Bulla-Broadmeadows Area.*

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Abstract.

The evidence provided by the chemical and mineralogical composition and the field occurrence of the kaolinised granodiorite is examined with a view to determining the most probable mode of origin of the deposits. The evidence now available, though inconclusive in itself, suggests that the kaolinising agencies might have been associated with the extrusion of the Tertiary basalts.

Introduction.

The occurrence of kaolinised granodiorite in the Bulla-Broadmeadows area has been noted by Dunn (1899), Armitage (1911), Stillwell (1911), and James (1920). The nature of the process which has given rise to irregular patches of kaolinised granodiorite, scattered over the surface of an otherwise normal intrusion, has been the subject of much discussion. Dunn and Armitage believe that the kaolin was produced by the action of meteoric waters, whilst Stillwell and James suggest that pneumatolysis was more probably responsible for the kaolinisation.

The most complete review of the evidence relating to the cause of kaolinisation was given by James (1920), who concluded that microscopical examination of the kaolinised material gave no definite evidence in favour of either of the above theories, but that "the field evidence, while producing little positive evidence in support of pneumatolysis, strongly discounts the meteoric theory."

The present paper contains the results of an examination of the physico-chemical characteristics of the kaolinised felspar and the associated minerals in an attempt to deduce the nature of the conditions under which kaolinisation took place. The evidence relating to the field occurrence of the altered material is then re-examined in order to decide the most probable way in which these conditions were brought about.

Field Occurrence of the Deposits.

GRANODIORITE.

The granodiorite outcrops in the Bulla district are so closely related, both chemically and mineralogically, to the neighbouring outcrops in the Broadmeadows district, that there is no reason to doubt the suggestion that they are both portions of the same igneous intrusion. Although chemical analyses quoted by James (1920) suggest that the granodiorite at Bulla contains slightly less potash and slightly more lime than the corresponding rock from Broadmeadows, and the orthoclase-plagioclase ratio of the latter caused Stillwell (1911) to term it an adamellite, the distinction has no significance as far as the present investigation is concerned.

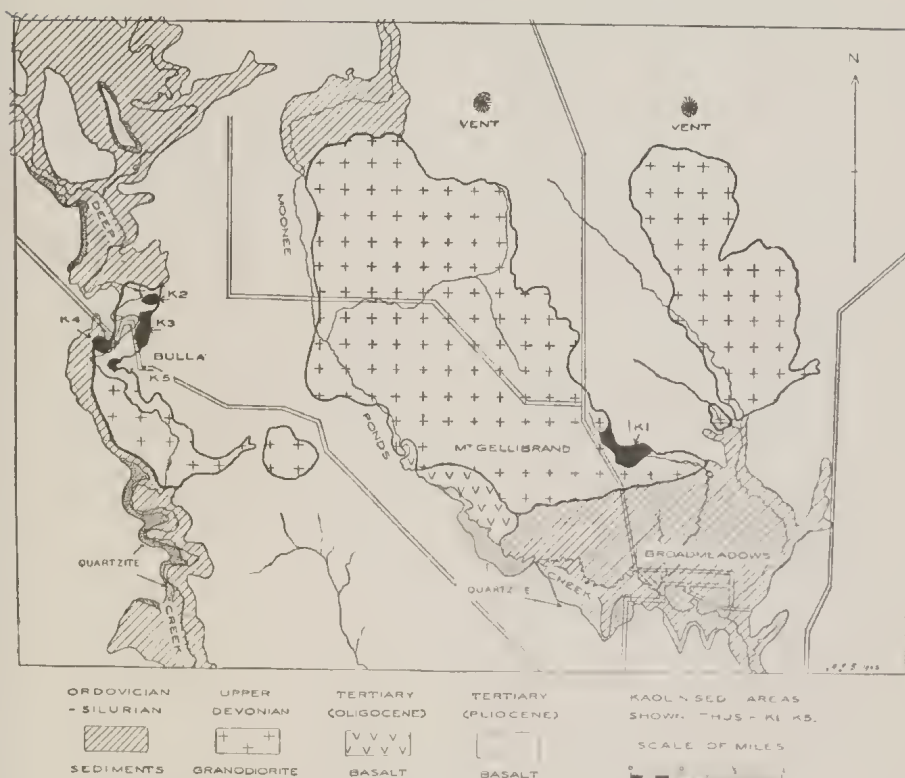
The geological map appended to this paper (p. 3) is based on a combination of the maps of Stillwell (1911) and James (1920), together with portions of Quarter Sheets 2 and 7 of the Geological Survey. It shows the Bulla-Broadmeadows intrusion as a stock-like body, elliptical in plan, extending about seven miles along its E.-W. axis, and about four miles along its N.-S. axis. On its northern, western, and southern boundaries, it junctions with contact metamorphosed Silurian and Ordovician sediments. Because of its analogies to similar granodiorites in Central Victoria, it is probable that the intrusion is of Upper Devonian age. The intrusion was exposed by erosion prior to the Tertiary, portion of it being covered during that period by fluvatile conglomerates, which were later covered by the basalts of the Older Volcanic series. Extensive lacustrine deposits separate portions of the Older Volcanic from the Newer Volcanic flows, a series of which have been extruded from vents near the western and northern boundaries of the area shown in the map (p. 3). The basalts of the newer Volcanic series extend across the granodiorite in two parallel tongue-like flows, leaving the central and two outer portions of the intrusion exposed as inliers standing up above the basalt flood. Post-Newer Volcanic erosion has exposed much of the western portion of the granodiorite that was originally covered with basalt.

KAOLINISED GRANODIORITE.

At Bulla, where the basalt has been removed by erosion, extensive outcrops of kaolinised granodiorite have been exposed, but no kaolinised granodiorite occurs above the surface level of the basalt.

It is not possible to trace definite connexions between the various kaolin outcrops here, since they are now separated by the valley of Deep Creek. There is a possibility that most of the present outcrops were originally joined to form a single large body of kaolinised material. However, the ridge of fresh granodiorite separating the kaolinised outcrops west of Deep Creek

(K4), from those to the east of the stream (K2, K3, K5) rises almost to the level of the basalt, so that any former connection between these two main kaolin deposits must have been but a shallow layer at the surface.



Geological Sketch Map of the Bulla-Broadmeadows Area.

Kaolinised granodiorite occurs at a high level (420 ft.) and at a low level (300 ft.), the maximum depth of kaolinisation in any single outcrop being about 90 ft., judging from the cliff exposures (K2) immediately to the north of the main bridge over Deep Creek. At this place, the kaolinised material at the bridge level is fresher in appearance than that at higher levels in the cliff, being blue-grey in colour, and containing numerous flakes of unaltered biotite and fragments of cloudy felspar. Completely kaolinised granodiorite can be observed to overlie fresher material in the valley wall of Deep Creek, where fresh granodiorite is

exposed at a spot 20 ft. below and 20 ft. to the west of, the floor of the kaolin quarry (K5) on the side road to Bulla School. About 60 feet of kaolinised granodiorite overlies fresh granodiorite in the gully (K4) across the creek from the school.

The upper surface of the kaolinised granodiorite is extremely well defined in some instances, the clean upper surface of the kaolin being in direct contact with the lower surface of the basalt. In other instances, 10 to 20 ft. of ferruginous grit and sand overlie the kaolinised material and are overlain by basalt. The latter has given rise to some silicification of the grits, converting them in part into quartzites. In the main road cutting at Bulla (near K3), the grits and sands contain small boulders of kaolinised and partially silicified granodiorite up to 6 inches in length, and markedly angular in form, showing facets, edges, and blunt points.

At Broadmeadows, a recently developed quarry (K1) in kaolinised granodiorite on the east flank of Mount Gellibrand was extending rapidly to the west and south when operations were suspended because of the war. The lateral extent of the kaolinised material is as yet unknown because of the thick soil covering to the east, west and south of the quarry. The kaolin is covered by basalt to the north and north-east, but can be traced round the boundary of the flow for several hundred feet to the north-west. The floor of the quarry is in kaolinised granodiorite at a level 20 ft. below the surface. Although the rock has been kaolinised for a distance of several hundred feet to the south of the basalt contact, the upper surface of the kaolinised material is, as at Bulla, below the upper surface of the basalt. In the main face of the quarry, the kaolinised material is divided into two parts by a vertical dyke-like body, containing only fine-grained quartz and kaolinite. The material is distinct from the surrounding kaolinised granodiorite, its appearance suggesting kaolinised quartz porphyry. The "dyke," which appears to strike approximately north-south, is from 10 to 20 ft. in thickness, and is exposed in the floor of the quarry for a distance of 40 ft. to the north, where it disappears under the basalt. Any southerly continuation is obscured by a thick soil layer. The contact between the dyke and the granodiorite is sharply defined, indicating that the intrusion of the dyke took place subsequent to the consolidation of the granodiorite and before the kaolinisation of the latter.

EXTRUSIVES.

In the area, the basaltic flows of the Newer Volcanic series can be divided into two groups, which James (1920) has termed the Upper and Lower series. At one place on the Sunbury-road, at the top of the rise from Bulla township, kaolinised granodiorite

is covered by a thin flow of basalt belonging to the Lower Series. The flow is honeycombed with vesicles up to an inch in length, indicating the presence of an abundance of gaseous material at the time of extrusion. A thicker flow of dense massive basalt, belonging to the Upper series, overlies this thin vesicular flow. Because of the absence of distinguishing characteristics which could be used to classify the various flows, there is as yet no consistent evidence connecting the occurrence of kaolinised granodiorite with any particular flow or group of flows.

Composition of the Deposits.

CLAY MINERALS.

In the hand specimen and under the microscope, there are no significant differences to be found in the appearance of samples of kaolinised granodiorite from any of the Bulla-Broadmeadows outcrops, with the sole exception of the material from the kaolinised "dyke" in the Broadmeadows Quarry, the fine-grained character of which suggests that quartz porphyry rather than granodiorite was the parent rock.

Thin sections show the normal kaolinised granodiorite to be composed of large (5-10 mm.) quartz grains, set in a matrix of kaolinite, bleached biotite, and muscovite, with minor amounts of zircon, calcite, and apatite.

The clay mineral, which is the most abundant mineral in the sections, occurs in irregular patches composed of book-like aggregates of minute flakes. These aggregates are elongated in the direction of the normal to the plane of basal cleavage, several of the more elongated "books" showing the sinuous curves of the characteristic "worm-like" aggregates of kaolinite described by Ross and Kerr (1930). Where the individual flakes are large enough to be observed, they show straight extinction, low birefringence, and a mean refractive index of 1.566. Indistinct interference figures suggest an optic angle (2V) of about 20°, the character being negative.

Since the minute grain size of the clay fraction militated against exact identification by optical means alone, the physical properties of the material were further investigated, as the exact identification of the predominant clay mineral has an important bearing on the problem of the nature of the conditions prevailing during the alteration of the granodiorite. The further properties on which the identification of the clay minerals was based were:

- (i) chemical composition
- (ii) dehydration curve
- (iii) adsorptive properties
- (iv) crystal structure.

(i) CHEMICAL ANALYSIS OF THE CLAY FRACTION.

Table II., Column IV., shows an analysis of the clay separated by sedimentation from the Bulla kaolinised granodiorite. The analysis suggests that a mineral of the kaolinite group forms the greater part of the material. The considerable amount of water expelled below 110°C. suggests that an appreciable amount of halloysite was present, as Ross and Kerr (1934) have shown that minerals of the halloysite type are capable of holding somewhat more water by "mechanical" bonds than are minerals of the kaolinite type. The proportion of halloysite to kaolinite indicated by the analysis (and in the dehydration curve) is, however, greater than that which prevailed in the samples as they were originally collected. This is a result of the sedimentation treatment necessary to remove quartz and mica, a portion of the kaolinitic clay fraction being separated in flake-aggregates which settle rapidly and are discarded with the fine quartz fraction.

(ii) DEHYDRATION OF THE CLAY FRACTION.

The various clay minerals of the kaolinite group lose their combined water at different and characteristic temperatures (Ross and Kerr, 1930). A check may thus be made on an identification by plotting the dehydration curve of the clay mineral. The clay fraction concerned in the present investigation showed a small, continuous loss of water between 110° and 450° (see fig. 1). At the latter temperature, a sudden loss in weight occurred, as is exhibited by kaolinite, little further loss occurred between 500° and 800°, so that it may be assumed that dickite and nacrite were not present in appreciable quantities.

(iii) ADSORPTIVE PROPERTIES OF THE CLAY FRACTION.

After separation from the altered granodiorite by sedimentation, the clay-fraction was treated with methylene blue to determine its adsorptive properties, and with malachite green to determine its base exchange capacity. The procedures are similar to those described by Faust (1940).

Methylene Blue.—About 0.1 gram of the clay fraction was agitated in a 1 per cent. aqueous solution of the dye, until no more dye was removed from the solution, which was then filtered off, the stained mineral being air-dried and examined under the microscope. All of the kaolin in the altered rock from Bulla and Broadmeadows was found to adsorb the dye strongly, the individual flakes being stained an intensely deep blue. When partially stained, the flakes retained a slight transparency and were feebly pleochroic from light to dark blue. The blue-grey polarisation colours of the flakes (viewed normal to the basal plane) appeared to be raised on staining to second order reds, as

described by Bosazza (1940). The colour appears to be distinct from the reddish reflection tint which the dye imparts to the surfaces of the flakes.

The above staining treatment established the clay mineral as kaolinite, as distinct from dickite and nacrite, which do not adsorb the dye to any appreciable extent. Montmorillonite and its analogues are not distinguished from kaolinite by this test, but show characteristic behaviour when treated with malachite green.

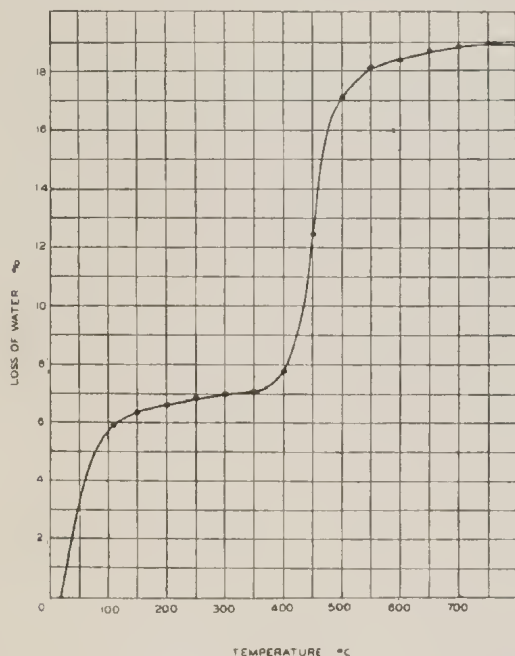


FIG. 1.—Dehydration Curve of Kaolin Mineral obtained from Kaolinised Granodiorite, Bulla (K 3).

Malachite Green.—The clay fraction was suspended in boiling dilute HCl for two hours, after which the acid was removed by filtration, and the residue washed free from acid. The washed mineral was then treated with a 1 per cent. neutral aqueous solution of malachite green, filtered, and allowed to dry. During such an acid treatment, clay minerals with replaceable cations form hydrogen substitution products which, when treated with the dye, inhibit the dissociation of the adsorbed malachite green. The particles are thus stained the yellow colour characteristic of the undissociated dye molecules. The clay mineral from the Bulla-Broadmeadows deposits showed behaviour characteristic of

the minerals of the kaolin group, i.e., the flakes were stained a deep blue-green by surface adsorption, with no indications of any base-exchange capacity.

It was found possible to stain bleached biotite to some extent with both the above stains, thereby providing a useful test for distinguishing this mineral from muscovite, which generally does not adsorb any appreciable quantity of the dye. Flakes of biotite showing a marginal rim of the bleached material are common in the less severely altered portions of the granodiorite, and these, when treated with the dyes, adsorb the dye in their bleached portions, the inner area of fresh biotite remaining unstained.

(iv.) X-RAY EXAMINATION OF THE CLAY FRACTION.

X-ray "powder" photographs of the clay-fraction from the Bulla-Broadmeadows kaolin outcrops indicated that the clay-mineral is kaolinite, thus confirming the identification made by the other methods described in this section.

Procedure.—The clay-fraction, separated by sedimentation, was air-dried at 20°C., mixed into a thick paste with collodion, and extruded from a fine-bore glass tube to form a rod about 1 mm. in diameter. When dry, the rod was mounted in a circular camera, 57.3 mm. in diameter, and exposed to filtered copper radiation for four hours. Line spacings were measured on the resultant film and are necessarily approximate because of the diffuse nature of the lines. The pattern agrees fairly well with that given by Kerr (1930) for kaolinite.

TABLE 1.

Arc in m.m.	Intensity.	Lattice Spacings A.U.
9.9	10	4.464
10.8	10	4.194
12.4	6	3.614
13.1	5	3.424
17.9	9	2.512
19.3	10	2.344
19.5	4	2.305
22.6	4	2.005
27.6	6	1.666
31.3	7	1.487
35.8	5	1.347
38.7	4	1.233

The line corresponding to the 1.487 spacing was relatively stronger and more diffuse than the same line in the photographs of kaolinite reproduced by Ross and Kerr (1930), suggesting that a certain amount of halloysite was present in the kaolinite from Bulla. Photographs of halloysite are characterised by a strong, diffuse line (1.510 AU) which almost coincides with the kaolinite 1.487 AU line. (Ross and Kerr, 1934).

ASSOCIATED MINERALS.

Quartz occurs in rounded grains, showing no signs of alteration from the original form of the mineral in the fresh granodiorite. A considerable amount of fine-grained secondary quartz is present in most kaolinised specimens, especially those which were obtained from outcrops immediately below the silicified sands and gravels which cover portion of the granodiorite.

Muscovite is present in both the kaolinised granodiorite and in the fresh rock. There is only a small quantity of sericite present, most of the particles being well-developed flakes from 0.1-1 mm. across.

Bleached Biotite.—Much of the biotite of the original granodiorite has undergone extensive decomposition into a colourless material which resembles muscovite, but may be distinguished from that mineral by optical and chemical means. Thus, the bleached biotite has a smaller optic angle ($2V$ about 10° - 20°) than muscovite ($2V$ from 30° - 40°). Flakes of the bleached biotite frequently retain some of the pleochroism of the fresh mineral, whilst the completely colourless material may be readily distinguished from muscovite by its capacity for the adsorption of dyes from dilute solution. It is possible that this adsorptive effect is partly due to the presence of finely dispersed kaolinite which would probably be produced to some extent during the bleaching of the biotite.

Since little information was available regarding the composition of bleached biotite, an attempt was made to determine its probable composition by spectrographically analysing an aggregate of flakes of the mineral selected under the microscope. The spectrograms obtained, when compared with those of normal biotite, showed that the bleached material contained much less iron and magnesium, and rather less manganese, titanium and nickel than normal biotite.

Accessory Minerals.—Heavy mineral concentrates from the kaolinised material contained zircon (common), garnet (rare) and limonite (rare). Baker (1942) recorded zircon and garnet in the fresh granodiorite.

CHEMICAL ANALYSIS OF THE KAOLINISED GRANODIORITE.

Table II. shows comparison analyses of fresh and kaolinised granodiorite from Mt. Gellibrand (Broadmeadows) and an analysis of the clay mineral (kaolinite with some halloysite), together with an analysis of the parent rock from which the clay has been derived. From columns I. and II., it can be seen that kaolinisation has been accompanied by a considerable loss of MgO , CaO , Na_2O and K_2O , the deficiency being made up by a corresponding increase in the content of chemically held water. The

amount of iron which has been removed is not great, but oxidation of ferrous iron to the ferric state has occurred to a large extent. The titanium content of the kaolinised material has increased by about 80 per cent., while most of the manganese has been

TABLE II.

	I.	II.	III.	IV.
SiO ₂	67.75	67.38	66.13	45.02
Al ₂ O ₃	16.11	16.21	16.83	35.85
Fe ₂ O ₃50	3.45	1.11	.99
FeO	4.00	.48	4.17	.24
MgO79	.29	1.83	.65
CaO	2.68	.71	3.26	1.76
Na ₂ O	2.60	.86	2.25	.03
K ₂ O	3.42	2.35	3.14	.25
H ₂ O+110°20	5.72	.23	8.90
H ₂ O-110°96	.88	1.68	5.90
CO ₂	Nil	Tr.	Tr.	Tr.
TiO ₂85	1.40	Tr.	.57
P ₂ O ₅09	.07	Tr.	Tr.
MnO	Tr.	.02	.07	Tr.
Cl	Tr.	Tr.	Tr.	Tr.
	99.95	99.82	100.70	100.16

I.—Adamellite, Mt. Gellibrand. (Analyst: H. C. Richards) (James, 1920).

II.—Kaolinised Granodiorite, Mt. Gellibrand. (Analyst: A. J. Gaskin).

III.—Granodiorite, Bulla. (Analyst: F. Watson) (James, 1920).

IV.—Clay-fraction, Bulla. (Analyst: A. J. Gaskin).

removed from the altered rock. All of the above changes in composition are typical of the processes of weathering and leaching by meteoric waters, the kaolinisation of the granodiorite having rendered the granodiorite porous and particularly subject to supergene attack. The removal of such components as magnesia, lime, soda, potash, and, to some extent, iron, in the form of their soluble bicarbonates and chlorides, is to be expected in the case of an igneous rock, such as the Bulla-Broadmeadows granodiorite, which has been mechanically broken up by decomposition and exposed to atmospheric attack. The fixation of titanium in the form of the insoluble hydrated titanium oxide known as leucoxene (Edwards, 1942) is a process common in such residual products of supergene weathering as clays, bauxites and laterites. Adsorption of hydrated titanium compounds, or lattice replacement of aluminium by titanium, might account for the considerable amount of TiO₂ (0.57 per cent.), associated with the fine clay which was separated from the kaolinised granodiorite by sedimentation (Table II., Column IV.). Since there is no visible rutile or ilmenite present in the kaolinised rock, the 80 per cent. increase in its TiO₂ content must be ascribed to the presence of secondary compounds, such as leucoxene, derived from ilmenite in the original rock by the action of the solutions engaged in leaching the kaolinised masses, or from titanium-bearing solutions accompanying the extrusion of the basalts.

SPECTROGRAPHIC ANALYSIS OF KAOLINISED GRANODIORITE.

Pneumatolytic action is generally accompanied by the introduction of various metallic elements into the rock body which is being attacked, though it is theoretically possible for pure water vapour, associated with mineral acids, to cause "pneumatolytic" alteration of certain minerals. It has been suggested (James, 1920), that the kaolinisation of the Bulla granodiorite was connected with the intrusion of the small tourmaline-aplite veins which occur in the granodiorite. Pneumatolytic action associated with the introduction of tourmaline is of a particularly intense nature, being commonly associated with the introduction of certain characteristic elements such as tin, tungsten, and boron. An attempt was therefore made to detect the presence of these elements in the kaolinised granodiorite, particularly in the neighbourhood of the tourmaline-aplite veins.

Spectrographic analysis was chosen as the means of determining the relative amounts of minor elements present in the fresh and kaolinised granodiorite, firstly because of the great sensitivity of the method, and secondly because of the impossibility of predicting in advance exactly which elements would show significant variations, and then applying suitable chemical spot tests. Spectrograms were taken on a Hilger "medium" quartz spectrograph, the region 2,000-4,000 ÅU extending the length of a 10-in. x 4-in. photographic plate. To obtain maximum sensitivity, the method of cathodic excitation in a low-voltage direct-current carbon arc (Strock, 1936) was used. Identification and intensity matching of lines were facilitated by the use of a projection densitometer, fitted with a ground glass screen and movable iron-arc and wavelength scale, constructed by the author on the lines of the projection micro-photometer described by Dietert and Schuch (1941).

Procedure.—Specimens weighing about 50 grams were selected from the various kaolinised outcrops and were treated so that representative samples, weighing no more than 20 milligrams, were obtained. In preliminary experiments, the large samples were crushed to -50 mesh, in an agate-mortar, and successively quartered until a sample weighing about 1 gram was obtained. This was crushed as finely as possible in a clean agate mortar, thoroughly mixed, and divided into minute samples for arcing. It was found necessary to burn the arc for one to two minutes at 8 amps. in order to volatilise a 20 milligram sample, which was therefore the maximum practical sample size, as complete volatilisation is necessary in an investigation which purports to compare the compositions of heterogeneous samples.

A series of spectrograms taken from samples prepared by the above method showed appreciable variations in the relative amounts of elements present, although the samples were selected

from the same "gram sample." The variations were undoubtedly due to the presence of relatively large particles of certain minerals in the samples (particularly biotite, which is extremely resistant to crushing beyond a certain grain size). Other defects of this method of sample preparation and excitation were the heavy background due to the excitation of silicon oxide molecules, and the long period of arcing necessary to volatilise the persistent globules of molten silicates which formed in the arc crater of the lower electrode, the long exposure intensifying the cyanogen band spectrum, which obliterates the fainter lines above 3380 A.U. on the spectrogram.

In order to overcome the above disadvantages, a sampling procedure was developed in which the original large rock samples were treated with hydrofluoric and sulphuric acids (5:1 mixture), the solutions evaporated, ignited, and leached with concentrated hydrochloric acid. The resulting solutions were evaporated to liquids of syrupy consistency, from which small samples were taken and volatilised in the arc. It was necessary to start the arc at a low current (3 amperes) and to maintain this current until the liquid in the sample had been vaporised, after which it was possible to increase the current to 10 amperes, without generating a large quantity of steam in the sample and thereby blowing it from the crater. In this method, the elements are vaporised in the form of their chlorides, which produce clearer and more intense spectra, completely free from the silicon oxide band spectrum. The relative volatility of the chlorides results in the complete volatilisation of the sample within a one-minute arcing period. Successive spectrograms taken by this method showed a high degree of consistency, coupled with a greater sensitivity than had been obtained by arcing the powdered minerals alone.

Spectrograms were taken with a Hoffmann diaphragm fitted over the spectrograph slit, so that three successive spectrograms could be photographed on any section of the plate. The uppermost of the series was always made an iron arc comparison spectrum indispensable in calculating the wavelength of the lines in the lower spectrograms, which were taken from kaolinised and normal granodiorite, respectively. In no instance did lines of any trace element consistently appear in the spectrograms of the kaolinised material, without appearing to the same (or greater) extent in the fresh granodiorite. Among the trace elements appearing in the spectro-analyses were boron, zirconium, nickel, and vanadium. The relative amounts of the major elements in the fresh and kaolinised granodiorite, as shown in the spectrograms, corresponded with the values shown in the chemical analysis (Table II.).

The Origin of the Kaolinisation.

MINERALOGICAL EVIDENCE.

There are certain facts in the mineralogical data presented above which have a bearing on the problem of the origin of the kaolinised deposits. These facts are concerned with the type of clay mineral, the nature of the associated alteration products, and the presence or absence of pneumatolytic elements in the deposits.

(1) The clay mineral in all the kaolinised portions of the area has been shown (above) to be kaolinite, the clay mineral characteristic of low-temperature kaolinisation (Ross and Kerr, 1930). Dickite and nacrite, the kaolin minerals formed under hydrothermal and pneumatolytic conditions, respectively, are absent from the Bulla-Broadmeadows deposits, indicating that the temperature of kaolinisation was not high, probably not above 100°C. The fact that kaolinisation has taken place is in itself an indication of the presence of acids or acid gases at the time of alteration. The kaolinising action of carbonic acid has been demonstrated by Parsons (1923), that of hydrochloric acid by Schwarz and Trageser (1933), and by Gruner (1939), and that of sulphuric acid by Anderson (1935). Although much hydrofluoric acid would probably have been present if the alteration were pneumatolytic, Gruner (*loc. cit.*) has shown that this acid has apparently no kaolinising action. It is generally reported that lignic acids produced in swamp deposits have a definite kaolinising action on granitic rocks, even at normal atmospheric temperatures.

(2) From a comparison of the mineralogical features of the fresh and kaolinised granodiorite, it can be deduced that the changes that have taken place during alteration are:—kaolinisation of all feldspar and some of the biotite and sericite, bleaching of most of the biotite, and production of some secondary muscovite.

Bleaching of biotite appears to be a weathering process involving the action of acids, as a similar bleaching effect can be produced by digesting the fresh mineral in hot dilute hydrochloric acid. The usual chloritic products of the atmospheric weathering of biotite are common in the solid granodiorite at Bulla and Broadmeadows, but do not occur in the kaolinised portions of the intrusion. Further evidence regarding the low-temperature nature of the alteration is provided by the absence of large quantities of muscovite or sericite from the kaolinised material. Gruner (*loc. cit.*) has shown that, in the presence of potash, kaolinite reverts to sericite at temperatures above about 400°C., so that this figure could be set as the probable upper limit of the kaolinisation temperature in this instance.

(3) The absence of pneumatolytic elements from the kaolinised granodiorite has been demonstrated (above) by comparing spectrographic analyses of the kaolinised material with those of

the fresh rock. The result supports the mineralogical evidence regarding the absence of pneumatolytic minerals from the kaolinised granodiorite. However, a serious limitation of the spectrographic method is the impossibility of detecting the presence of the negative radicals which would probably be introduced during the kaolinisation. The application of chemical tests to the kaolinised material showed that small quantities of the carbonate and chloride radicals were present but that the sulphate radical was not present in detectable amounts. Since the radicals detected are normally present in traces in all rocks exposed to atmospheric attack, their presence in this instance is of no significance in the determination of the cause of kaolinisation. A simple comparison between the relative amounts of such radicals in the fresh and in the altered rock is not possible because of their great difference in physical character. The high porosity and adsorptive capacity of the kaolinised material would naturally result in a higher concentration in it of carbonic acid and sodium chloride derived from the atmosphere, whilst the porosity of the material would permit of the ready escape of any concentration of a soluble salt or acid introduced during pneumatolysis.

Zircon is present in equal amounts in both fresh and kaolinised granodiorite, and shows no significant alteration effects. Comparison of heavy mineral concentrates prepared from fresh and kaolinised material indicated that no "pneumatolytic" minerals such as tourmaline or topaz had been introduced during kaolinisation.

The evidence provided by the minerals associated with the kaolinite is thus in agreement with the evidence in (1) above, i.e., leading to the conclusion that kaolinisation took place in an acidic environment at a temperature between 0°C. and 400°C., in the absence of any appreciable quantities of foreign metallic elements. Such conditions could have been brought about by the action of:

(a) Acidic liquids or gases associated with the final cooling phases of the solid granodiorite, the composition of the kaolinising agency being limited to a relatively pure acidic material containing few or none of the elements usually associated with pneumatolytic or hydrothermal attack. No mineralogical evidence could be found to support the idea that kaolinisation was due to "pneumatolysis" in the accepted sense of that term. However, the nature of the altered material is rather more compatible with the milder "hydrothermal" attack.

(b) Acidic liquids produced in swamp deposits on the granodiorite surface, prior to the extrusion of the Tertiary basalts.

(c) Acidic liquids or gases associated with the extrusion of the overlying basalts, either included in gaseous form in the flows themselves, or dissolved in the meteoric waters accompanying the eruption.

Since any one of the above agencies could have produced the mineralogical and chemical features of the deposits, the field evidence must be relied upon to decide which is the most probable hypothesis.

FIELD EVIDENCE.

Kaolinisation of the granodiorite subsequent to, or immediately preceding, the extrusion of the Tertiary basalts would have had little or no influence on the physiographic development of the area, because of the protective covering afforded by the extrusives. The fact that the kaolinisation has had no apparent influence on the physiographic development of the area in either pre-basaltic or post-basaltic time is thus strong evidence in favour of the idea that kaolinisation did not take place before the development of the land surface on which the basalts were extruded. This evidence thus opposes the "pneumatolytic" theory. There are numerous indications that the kaolinised areas have had no apparent influence on the form of the pre-basaltic land surface. Among them is the fact that within a distance of a few hundred yards, there is a difference of over a hundred feet in the elevations of the upper surface of the main kaolinised outcrop at Broadmeadows, and the upper surface of the deposit lying to the south (see Section I.). It is a significant fact that the surface of the lower outcrop shows a particularly clean-cut junction with the overlying basalt, and does not exhibit the disturbed and re-distributed appearance of a valley floor cut in kaolinised material.

If kaolinisation had long preceded the extrusion of the basalt, sedimentary clay deposits representing re-distributed kaolinised granodiorite would probably have been formed. No such sediments are known, the nearest clay deposits (at Campbellfield) being post-basaltic.

With regard to the angular boulders of kaolinised material at Bulla, it seems probable that the kaolinised granodiorite was too friable to have retained such shapes, which are, however, characteristic of boulders of fresh granodiorite. This suggests that the kaolinisation of the boulders in the grit took place after the deposition of the grit, presumably by some agency associated with the extrusion of the overlying basalt. A search among boulders in the grits and sands above some of the kaolin outcrops failed to reveal any fresh unaltered granodiorite.

It has been suggested (James, 1920) that the shape of the kaolinised masses at Bulla is that which is characteristic of kaolin deposits produced by pneumatolysis, but in no case was it found possible to substantiate this statement in the field, as the boundaries of the kaolinised masses are not exposed to any extent in the quarries and gullies. All that can be established with certainty is the fact that the kaolinised masses do not increase rapidly in extent with increase in depth, a point which can be deduced

from the occurrences of fresh granodiorite below and at the sides of kaolinised outcrops (K.3), (K.4) and (K.5).

The presence of tourmaline veins in the kaolin quarries on the east bank of Deep Creek has been quoted by James (1920), as positive evidence of pneumatolysis in connection with the kaolinisation. One vein occurs in each quarry, and a similar vein, passing through practically unaltered granodiorite, is now exposed in the floor of the gully on the western side of Deep Creek. All of the veins have a maximum thickness of about 1 inch, and show sharp boundaries with the surrounding rock. In structure, the veins resemble fine-grained pegmatites, as they contain relatively large crystals of tourmaline, quartz and fresh feldspar. The presence of the fresh feldspar could be explained, if kaolinisation were due to the action of acidic liquids percolating down from above, by assuming that the compact nature of the veins protected the feldspar. If it is assumed that the veins acted as feed channels for the kaolinising agencies, as they would have done if kaolinisation were due to pneumatolysis associated with their intrusion, it becomes difficult to account for the fact that the feldspar which they contain is not even partially altered.

A suggestive point in the evidence is the fact that nowhere in the area does the kaolinised material occur above the level of the basalt surface, although in several places the upper limit of kaolinisation is almost on the same level as the surface of the basalt. There are no kaolinised exposures in those portions of the granodiorite which have been removed from contact with either the basalt itself, or solutions accompanying the basalt.

At Broadmeadows, no evidence could be found to support the suggestion that kaolinisation was in any way connected with the intrusion of the dyke-like body. There is no quantity of tourmaline or any other mineral associated with pneumatolysis in it or in any part of the quarry, and there are no signs of disturbance along the contacts of the dyke with the surrounding granodiorite such as would be expected if the dyke had acted as the plane of weakness along which the kaolinising agencies had moved. No variation in the degree of kaolinisation of the surrounding granodiorite could be found within the limits of the excavation, which extends at least 70 feet in either direction at right angles to the strike of the dyke.

DISCUSSION.

The three possible modes of origin suggested by the mineralogical evidence may now be reviewed in the light of the above field evidence.

(a) Kaolinising agencies associated with the intrusion of the granodiorite would have to have been of an unusual type to comply with the mineralogical evidence discussed above. The only obvious way in which lime, magnesia, and alkalis could have been completely removed from the fresh rock, would seem to be

the contact of percolating waters with the solid granodiorite in the final cooling stage of the intrusion. It is becoming increasingly evident that there are very few definite instances of kaolinisation by agencies associated with the parent intrusions, there is even reason to doubt the evidence at Cornwall (Collins, 1909), which has long been cited as the classic example of "pneumatolytic" kaolinisation (Ross and Kerr, 1930). In the present case, the absence of minerals and trace elements typical of pneumatolytic and hydrothermal action, the nature of the clay minerals formed during the alteration, and the various points quoted in the field evidence (above) are considerable obstacles to the development of the theory.

(b) Kaolinisation due to the action of natural waters containing organic acids derived from decomposing vegetation in swamps is a recognised process (Kerr, 1930), and one which could have given rise to the mineralogical and chemical associations of the Bulla-Broadmeadows deposits. Field evidence, however, opposes the hypothesis, since it opposes the idea of pre-basaltic kaolinisation. The only favourable evidence available is the fact that James (1920) has shown that lacustrine deposits containing plant remains, occur between the Silurian bedrock and the overlying basalts in parts of the Bulla district. It is not improbable that similar deposits formerly occurred in depressions in the surface of the granodiorite and gave rise to acidic solutions which penetrated and kaolinised the underlying granodiorite during the period immediately prior to the extrusion of the basalts. Pre-basaltic erosion might account for the absence of the sediments from the neighbourhood of most of the kaolinised masses at present exposed.

(c) Although there is no conclusive evidence for the hypothesis that assigns the kaolinisation to the effect of acidic liquors associated with the extrusion of the basalts, the theory suffices to explain the mineralogical and chemical characteristics of the kaolinised masses, and is in accord with the available field evidence. There is no evidence in opposition to the idea, the only point raised by James (1920) being the fact that fresh granodiorite underlies the basalt in two places. This evidence seems rather to be directed against the idea that kaolinisation was brought about by the direct heating action of the molten basalt, a factor which it is certain would have played little or no part in the kaolinisation, because of the low thermal conductivity of the granodiorite, especially if dry. A more probable mechanism is that in which acid vapours, evolved during the extrusion of the basalts, dissolved in the magmatic and meteoric waters accompanying the event, and formed acidic solutions. The latter trapped up against the edges of the lower-lying basalt flows, from there penetrated beneath the basalts and caused the kaolinisation of the under-lying granodiorite. Such alteration would be

localised in limited areas, the location of which would be determined by a number of independent variables, such as relative altitude, permeability, temperature of the flows and solutions, and the various drainage factors which would control the collection and distribution of the active liquids

Conclusion.

SUMMARY.

The conditions under which kaolinisation took place can now be postulated with some certainty, but there is insufficient positive evidence available to permit of a definite decision being made in favour of any one of the three probable modes of origin. Although there is no conclusive evidence to discount the possibility of kaolinisation being due to agencies associated with the intrusion of the granodiorite, or to solutions produced in overlying swamp deposits, the evidence in favour of these theories is not as convincing as that which supports the view that the kaolinisation was connected with the evolution of acidic liquors and gases accompanying the extrusion of the Tertiary basalts.

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